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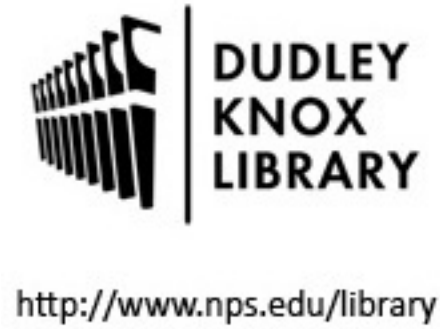

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AN INVESTIGATION OF THE PROPERTIES AND REACTIONS OF PERCHLORYL FLUORIDE INCLUDING A NEW REACTION

O. CLARKE CHISUM

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* * * * *

O. CLARKE CHISUM

AN INVESTIGATION OF THE PROPERTIES AND REACTIONS OF PERCHLORYL FLUORIDE INCLUDING A NEW REACTION

by

O. Clarke Chisum

Lieutenant, United States Navy

Submitted in partial fulfillment of
the requirements for the degree of

MASTER OF SCIENCE
IN
CHEMISTRY

United States Naval Postgraduate School
Monterey, California

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ABSTRACT

Perchloryl fluoride, developed by Pennsalt in 1952, takes part in many and varied reactions to yield interesting and useful products. A compilation of physical, chemical and toxicological properties is presented. Those reactions already established are discussed, as are several the author attempted, including a new reaction dependent upon the oxidizing properties of perchloryl fluoride. Several reactions which were considered but not attempted because of time limitations are included.

The writer wishes to express his appreciation to Dr. Robert Boschan of the United States Naval Ordnance Test Station, China Lake, California under whose guidance the majority of this study was undertaken, also to Professor George H. McFarlin and Professor John W. Schultz of the United States Naval Postgraduate School for their assistance.

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1. Introduction.

Perchloryl fluoride was first synthesized by Englebrecht and Atzwanger of Pennsalt Chemicals Corporation, Philadelphia, Pennsylvania in 1952 [1]. In this unique compound, oxygen, fluorine, and chlorine, the most electronegative of elements, are found combined in a stable, yet chemically active molecule. This stability can be attributed to the molecular symmetry of the tetrahedral configuration. The central chlorine is surrounded by the three oxygen atoms, and the one fluorine atom. This configuration is strongly supported by spectrographic evidence [2], and chemical behavior.

Uses of perchloryl fluoride investigated to date are generalized as follows [8]:

Oxidant: powerful, yet controllable.

Cutting and welding: Faster rate of cutting than oxygen under same conditions, and at lower pressure than generally used for oxygen.

Dielectric gas: Perchloryl fluoride gas has a high dielectric strength, which, in contrast to other gases is only slightly effected by radiation. Additional advantages are suppression of corona discharge and elimination of "glow".

Medicine: Protection against radiation sickness and destruction of food infecting bacillus.

Pyrotechnics and explosives: When absorbed on porous materials, perchloryl fluoride is explosive.

Metal processing: Perchloryl fluoride destroys cyanide residues in electroplating operations.

Petroleum refining: Perchloryl fluoride is an effective desulfurizer for lubricating oils and petroleum fuels.

Chemical intermediates: Discussed in Sections 5, 6, 7 and 8, this paper.

2. Physical Properties.

The physical properties of perchloryl fluoride are presented in the following compilation [8].

Formula	ClO_3F
Molecular Weight	102.5
Color: Gas	Colorless
Liquid	Water-white
Odor	Characteristic, sweet
Melting Point	Minus 146 ± 2 °C
Boiling Point	Minus 46.8°C
Density: Gas @ Tc;Pc	0.637 g/ml.
Liquid @ 20°C	1.434 g/ml.
Critical Temperature	95.17 ± 0.10°C
Critical Pressure	53.00 atm.
Critical Density	0.637 g/ml.
Heat of Vaporization	4.6 kcal/mole
Trouton Constant	20.4 cal/deg. mole
Dipole moment	Less than 0.03 Debye units
Viscocity of Liquid	
Minus 80°C	0.620 cp
0°C	0.219 cp
60°C	0.139 cp
Vapor Pressure	
0°C	86.12 psia
25°C	176.06 psia
50°C	322.03 psia
Heat of Formation	
Gas @ 25°C	Minus 5.12 ± 0.68 kcal/mole
Cp/Cv @ 24°C	1.12 ± 0.01
Entropy: Gas @ 25°C	66.51 cal/deg.mole (calc'd)
Specific Heat of Liquid	
Minus 40°C	0.229 cal/g°C.
Minus 10°C	0.244 cal/g°C.
Plus 50°C	0.290 cal/g°C.

It is reported that the density of liquid perchloryl fluoride in equilibrium with its own vapor obeys the following equation over the temperature range of -142°C. to 54°C [5]:

$$\text{Density (g/ml)} = 1.088 - 7.280 \times 10^{-4} T + 6.455 \times 10^{-2} (T_c - T)^{1/2}$$

T in degrees Kelvin

The vapor pressure of perchloryl fluoride may be calculated from the following equations over the specified temperature ranges [3]:

Minus 120°C. to minus 40°C.

$$\text{Log}_{10}P \text{ (mm of Hg)} = 18.90112 - 1443.467 \times T^{-1} - 4.0957 \log_{10}T$$

Minus 40°C to critical temperature 95.17°C.

$$\text{Log}_{10}P(\text{atm}) = 4.46862 - 1010.814 \times T^{-1}$$

(T in degrees Kelvin)

Data on viscosity of perchloryl fluoride were fitted by Simkin and Jarry [4] to an equation covering the range from minus 80 to plus 60°C. Results obtained experimentally show an average deviation of 1.7% from that obtained from the equation [3]:

$$\text{Log}_{10}\ n = 299/T - 1.755$$

(n = viscosity in centipoises)
(T = degrees Kelvin)

The six fundamental vibration frequencies in perchloryl fluoride reported by Lide and Mann [2] were also located during this investigation. It is noted that these six fundamental vibrations serve to support strongly the tetrahedral structure.

Description	Frequency (cm^{-1})
ClO-stretching	1061
ClF-stretching	715
ClO_3-deformation	549
ClO-stretching	1315
ClO_3-deformation	589
Rocking	405

3. Toxicity and Handling [10].

Perchloryl fluoride is moderately toxic, forming methemoglobin in the body and destroying the red blood cells causing anemia, anorexia and cyanosis. Recovery is usually rapid, with no permanent physiological damage. Perchloryl fluoride can be absorbed through the skin. Its odor

can be detected in concentration as low as 10 parts per million, however this should not be relied upon as indication of toxic concentration in air. The chronic effects are unknown. The liquid can cause frost-bite-like wounds.

Perchloryl fluoride presents a moderate fire hazard, however, while nonflammable, it will support combustion.

Explosion hazard is moderate. Some substances such as lampblack, sawdust, hydrogen sulfide and charcoal yield explosive mixtures as low as -78°C.

During the course of this research it became necessary to determine the impact sensitivity of perchloryl benzene. This test was carried out on a standard type impact tester using a two kilogram weight, one drop of perchloryl benzene, and small glass helix in a metal test cup. It was determined that perchloryl benzene detonated with considerable black smoke and orange flash one hundred percent of the time when the weight was dropped from a height of two and one-half centimeters (the lower limit of the testing device). For comparison, the height of drop for fifty percent detonation for nitroglycerine is three centimeters, while that for TNT is 165 centimeters as determined on comparable devices. The result obviously dictates extreme caution.

It is recommended that hood, shield, and eye-glasses be used habitually while experimenting with perchloryl fluoride. The effect of perchloryl fluoride on many specific materials and its corrosive effect are given in Pennsalt Chemicals Technical Division Booklet DC-1819, pp. 13-17. It is noted that valves suitable for use with oxygen are satisfactory except that two-stage regulators are not necessary.

4. Chemical Properties [8].

In contrast to chloryl fluoride (ClO_2F) and fluorine perchlorate (ClO_4F), perchloryl fluoride is both chemically and physically stable. Perchloryl fluoride is thermally stable up to 500°C. It is only slightly hydrolyzed by water, although concentrated alkali metal hydroxides (sealed tube) cause quantitative hydrolysis of perchloryl fluoride to perchlorate and fluoride ions. A quantitative determination of perchloryl fluoride may be made by hydrolysis with alcoholic potassium hydroxide to produce potassium perchlorate precipitate and soluble potassium fluoride.

A general pattern of reactivity was reported [6]. The relative order of reactivity appears to follow the base strength of the organic reactant with the strongest bases reacting most readily. Nucleophilic groups react readily with perchloryl fluoride. It reacts with metallo-organic compounds especially when the metallic atom is bonded to carbon through a different atom, e.g., oxygen. The presence of a halogen-metal bond as in a Grignard reagent facilitates reaction with perchloryl fluoride.

5. Reactions--General[8].

From the work done at Pennsalt it appears that there are five general classes of reactions in which perchloryl fluoride will take part. The following is a compilation of these reactions, with examples of each.

Oxidation: Oxidation reactions with perchloryl fluoride are controlled by pH, temperature, and concentration of reactants. Rate increases with temperature, and may become explosive. Perchloryl fluoride and hydrogen sulfide are explosive in a 1:1 ratio (volume)

at 150°C, but when in high dilution, hydrogen sulfide is oxidized according to:

$$3ClO_3F + 4H_2S = 4SO_2 + 3HF + 3HCl + H_2O$$

The following oxidation of hydrogen chloride in the gas phase takes place between 200-300°C:

$$ClO_3F + 7HCl = HF + 4Cl_2 + 3H_2O.$$

Nitrite, sulfite, and cyanide ions are oxidized to nitrate, sulfate, and cyanate ions respectively. Metallic ions are usually oxidized from lower to higher oxidation states, and some inorganic salts, e.g., alluminum chloride undergo strongly exothermic reactions with perchloryl fluoride. Organic compounds such as mercaptans, aldehydes, and many nitrogen containing compounds react with perchloryl fluoride. In the vapor phase nearly all organic compounds appear to be oxidized to give acid and/or aldehyde products. These reactions may proceed explosively.

Ammonolysis: Perchloryl fluoride reacts with ammonia to yield the ammonium salt of perchlorylamide $(ClO_3NH)^-(NH_4)^+$ which can be reacted with silver or barium compounds to give the metallic salt. These salts are very sensitive when dry, and may detonate.

$$ClO_3F + 3NH_3 = NH_4F + ClO_3NH \cdot NH_4$$

$$ClO_3NH \cdot NH_4 + AgNO_3 = NH_4NO_3 + ClO_3NH \cdot Ag$$

Fluorination: Perchloryl fluoride is a ready means of fluorinating compounds with a replaceable hydrogen atom, as in malonic esters and acetoacetic esters to give the dialkyl difluoromalonates and diakyl difluoroacetoacetates. Monofluoronated products result from using C-alkylated malonates.

$$2ClO_3F + Na_2C(CO_2R)_2 = CF_2(CO_2R)_2 + 2NaClO_3$$

Perchlorylation: Benzene may be perchlorylated in accordance with the following reaction.

$$C_6H_6 + AlCl_3 + ClO_3F = C_6H_5ClO_3 + AlCl_2F + HCl$$

Etherification: Inorganic esters result from the reaction of perchloryl fluoride with alkoxides. These esters further react with the alkoxide to produce the corresponding ether. If the alkyl group is highly acidic (e.g., tri-fluro-ethyl), the intermediate alkyl perchlorate can be isolated.

$$ClO_3F + RONa = (R\text{-}O\text{-}ClO_3) + NaF$$

$$(R\text{-}O\text{-}ClO_3) + R\text{-}O\text{-}Na = R\text{-}O\text{-}R + NaClO_4.$$

6. Reactions--Previously Reported *[6] [7]*.

Perchloryl benzene. It is suggested that perchlorylation of the aromatic ring takes place in a manner analogous to that of a Friedel-Crafts reaction. In the absence of aluminum chloride no reaction takes place between perchloryl fluoride and benzene. However, when aluminum chloride (aluminum bromine or other similar catalyst) is present, with excess benzene as a solvent, the reaction mixture becomes black, upon the addition of perchloryl fluoride and there is considerable evolution of hydrogen chloride and heat. After approximately one mole of perchloryl fluoride has reacted per mole of aluminum chloride the reaction becomes very slow and stops. In this way the reaction differs from the conventional Friedl-Crafts alkylation in which the catalytic aluminum chloride is recoverable. The product, perchloryl benzene is a colorless liquid, b.p. 232°(78° @ 2 mm).

In strong alkaline solution perchloryl aromatics are hydrolyzed to phenol and perchlorate ion. Hydrolysis of perchloryl benzene with

potassium hydroxide yields potassium perchlorate and a product with a melting point of 90-92° which when brominated showed no melting point depression when mixed with authentic sample of 2,4,6 tribromphenol.

3-Nitro perchloryl benzene. Perchloryl benzene may be nitrated with the conventional nitric acid-sulfuric acid nitrating mixture. This reaction demonstrates the stability of the perchloryl addition. Alkaline hydrolysis gives m-nitro phenol, and proof of the meta directing properties of the perchloryl group. Product is yellow crystals, m.p. 49-50°C.

3-Amino perchloryl benzene. Reduction of the nitro group to the amino group is readily accomplished with stannous chloride. Product is colorless needles, m.p. 30-31°C.

3-Perchloryl acetanilide. By using acetic-anhydride in glacial acetic acid the acetyl derivative of 3-amino perchloryl benzene was obtained. Product is colorless needles, m.p. 136-37°C. (See discussion under Section 7.)

4-Fluoro perchloryl fluoride. A method completely analogous to that for the perchlorylation of benzene. Product is light yellow oil, m.p. 28°C, b.p. 53° @ 0.25 mm.

2-5 Dimethyl perchloryl benzene. The perchlorylation of p-zylene proceeded with aluminum chloride, but resulted in poor yield. Product was colorless needles, m.p. 30-31°C.

It has also been reported that perchloryl fluoride reacts with strong organic bases, and that in the case of sodium salts of active methylene compounds that the reaction introduces fluorine into the

organic molecule. The following products have been reported synthesized to date *[7]*:

Diethyl 2,2 difluoromalonate
Difluoromalonamide
Ethyl 2,2 difluoroacetoacetate
5-ethyl-5-fluorobabrituric acid
Diethyl 2-fluoro-2-phenylmalonate

7. Reactions--Attempted in Connection with this Research.

Preparation of perchloryl naphthalene.

Because of the extreme sensitivity of perchloryl benzene (see Section 3), it was decided to attempt the perchlorylation of naphthalene, predicted to be a solid, and subsequently to determine its sensitivity. The synthesis was attempted three different times using carbon disulfide, nitro methane, and nitrobenzene as solvents, and aluminum chloride as "catalyst". All three reactions proceeded in a manner similar to that for the perchlorylation of benzene. After the evolution of hydrogen chloride ceased, reaction mixture was filtered to obtain an amber liquid and thick black tarry substance. No treatment thus far has produced the desired product from the filtrate. Extraction and steam distillation were unsuccessful. Vacuum distillation or sublimation were not attempted.

Preparation of 3-perchloryl acetanilide.

This synthesis attempted to add the perchloryl group to acetanilide directly by the Friedel-Craft type reaction. Evolution of heat and hydrogen chloride indicated that a reaction took place, however subsequent operations produced only recovered acetanilide as product. Note that the desired product was obtained as discussed in Section 6, but through an entirely different approach.

Reaction between perchloryl fluoride and succinimide.

It was thought that the product from this reaction might contain either the N-F, or the N-ClO_3 grouping. It was noted in this reaction that the reaction mixture remained clear, while in all others considerable cloudiness was observed. Although hydrogen chloride was detected initially, subsequent evolution was identified as chlorine gas. Both reaction mixture, and condensate in trap were brilliant green in color. The final product was a heavy jelly-like mass. Subsequent treatment failed to produce the desired product. Results were also negative when the reaction was carried out at a higher reflux temperature in acetic acid.

Reaction between potassium phthalimide and perchloryl fluoride.

This reaction was proposed and carried out on the premise that the potassium salt might be more reactive than phthalimide. Again, evolution of heat and hydrogen evidenced a reaction. Extraction of the filtrate for the reaction mixture with ether produced a sharply melting product. Comparison of spectrographic data, however, revealed that the desired product had not been obtained. See, however, Section 8.

Reaction between resorcinol dimethyl ether and perchloryl fluoride.

Reaction again apparent, but no product obtained.

8. A New Reaction.

As was noted in Section 7 the reaction between potassium phthalimide and perchloryl fluoride produced a product worthy of note. In considering this reaction it was noted that the desired product would probably contain either the N-F or the N-ClO_3 grouping, and result in the formation of potassium perchlorate or potassium fluoride respectively. Since both of

these products are incoluble in dimethyl sulfoxide, this compound was chosen as a solvent. The product obtained from the reaction gave a strong positive test for sulfur, and since it definitely was not the desired product, it appeared highly possible that the solvent had taken part in the reaction. Considering the oxidizing properties of perchloryl fluoride, a possible product, dimethyl sulfone was suggested. An authentic sample of dimethyl sulfone was prepared using a method analogous to that described for the preparation of tetramethylene sulfone [11]. Spectrographic analysis showed the two samples to be the same, and no depression in melting point was observed.

The procedure for the preparation of di-methyl sulfone from di-methyl sulfoxide is as follows. In a three-neck flask fitted with fritted gas inlet, stirrer and thermometer, dissolve 39 grams (0.5 mole) dimethyl sulfoxide in 300 cc. carbon tetrachloride and 3 cc. pyridine. Keeping reaction mixture between 20° and 40°C, add perchloryl fluoride (subsurface). Upon cessation of the evolution of hydrogen chloride as determined by litmus at the trap opening, filter white crystals and recrystalize from ether. Melting point 109° [12], yield 48%. By varying temperature, solvent and base catalyst, it is felt that the yield can be increased considerably. The conditions described above were the only ones followed during this preparation.

9. Reactions--Proposed.

The following reactions have been considered, but not attempted due to time limitations.

a. Reaction between resorcinol dimethyl ether and perchloryl fluoride.

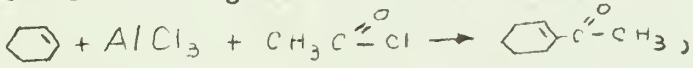
Two possible products, however suspect 3-perchloryl resorcinol dimethyl ether to predominate.

b. Reaction between bromo-succinimide and perchloryl fluoride.

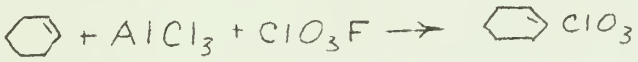
Possibly more reactive in this situation than the succinimide attempted earlier.

c. Reaction between cyclo-hexene and perchloryl fluoride.

Since the following reaction is well established

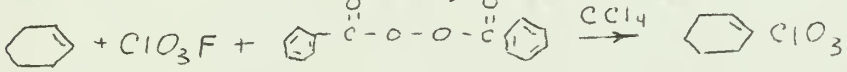


it is possible that the following reaction might take place,



The use of indene vice cyclo-hexene might result in a more stable product.

d. Reaction between perchloryl fluoride and cyclohexene in a reaction analogous to a Wohl-Ziegler bromination reaction [9].



EXTREME CAUTION is recommended in carrying out any reaction involving perchloryl fluoride due to the possible sensitive nature of the products. (See Section 3.)

e. Investigation of oxidizing properties of perchloryl fluoride.

1)

2)

10. Conclusions.

1. The direct substitution of the ClO_3^- on the already substituted ring by a Friedel-Crafts type reaction has failed in all attempts

indicating that this approach to substitute perchlorylated aromatics is not feasible by the methods as described.

2. The perchlorylated aromatic appears to be sufficiently stable to allow additional substitution on the ring, and subsequent reactions with these substituted groups (e.g., benzene to perchlorylbenzene to 3-nitro-perchlorylbenzene to 3-amino-perchlorylbenzene to 3-perchloryl acetanilide as discussed in Section 6.

3. The sensitivity and apparent brisance of perchlorylbenzene indicates that cautions investigation of perchlorylated products as explosives is feasible.

4. In instances where Cl^- or Cl_2 in products is of no particular consequence perchlorylation should be considered as a route to improving the oxygen balance of explosives and propellants.

5. Investigation of the possibility of perchlorylating certain polymers to be used subsequently as binders for propellants is suggested. The preparation of perchloryl styrene may prove of interest.

6. Investigators are again enjoined to observe all safety precautions. Both the sought-after products and products from unpredicted side reactions are likely to be extremely sensitive.

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